

ANTI-FOGGING FILM, AND SUBSTRATE WITH ANTI-FOGGING FILM

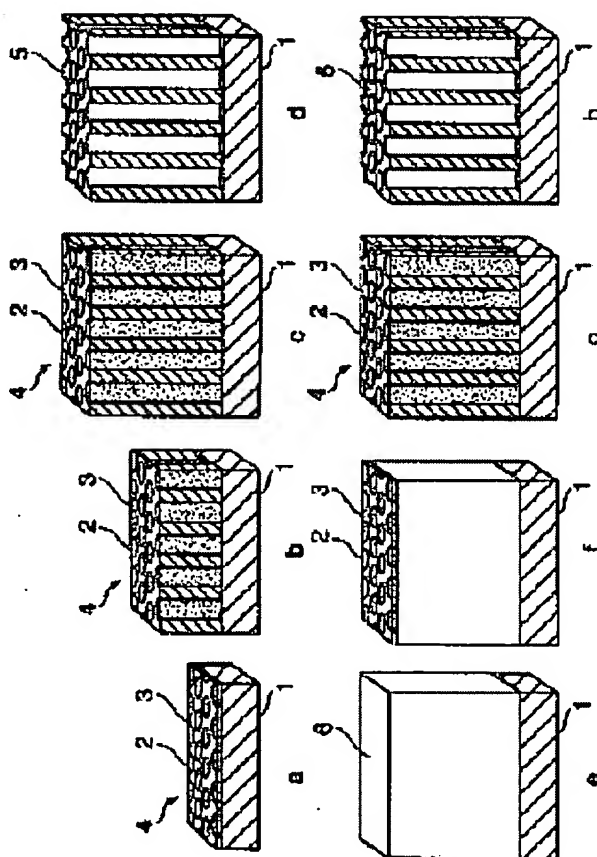
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Abstract of JP2001261376

PROBLEM TO BE SOLVED: To obtain an anti-fogging film having a high film strength and excellent adhesivity to a substrate.

SOLUTION: This anti-fogging film is formed by removing one-dimensionally grown columnar phases 2 from a composite film 4 consisting of a great number of the columnar phases 2 and a matrix phase 3 surrounding the columnar phases on a substrate 1 and has a great number of one-dimensionally penetrated pores enclosed by walls continuous from one surface of the film to the other surface and ≤ 30 deg. contact angle to water.



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CLAIMS

[Claim(s)]

[Claim 1] The anti-fogging film characterized by to be the anti-fogging film which has the pore of a large number which were surrounded with the wall which continues from one membranous front face to the front face of another side, and which are penetrated in single dimension formed on the base by removing the pillar-shaped phase which grew like a single dimension in the bipolar membrane which consists of a pillar-shaped phase of a large number which grew in single dimension, and a matrix phase which encloses it, and for the contact angle over water to be 30 degrees or less.

[Claim 2] The anti-fogging film according to claim 1 with which said anti-fogging film consists of one or more sorts chosen from an oxide, carbide, the boride, the nitride, and the metal.

[Claim 3] The anti-fogging film according to claim 1 or 2 whose average aperture of said pore penetrated in single dimension is 1-500nm.

[Claim 4] The anti-fogging film according to claim 1, 2, or 3 whose specific surface area of said anti-fogging film is 20-2000m²/g.

[Claim 5] The base with an anti-fogging film which has an anti-fogging film according to claim 1, 2, 3, or 4 on a base.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Field of the Invention] This invention relates to an anti-fogging film with the pore (henceforth single dimension penetration pore) penetrated in single dimension. In detail, it can use suitably as anti-fogging films for cloudy prevention, such as a windowpane, a mirror, or an optical lens front face, and is related with the anti-fogging film which has high endurance.

[0002]

[Description of the Prior Art] If the mirror of a bathroom or a washstand touches the air which contains a steam so much, the waterdrop of wavelength extent of light or the magnitude beyond it adheres to a front face, scattered reflection of the light will be carried out by the waterdrop, and the overcast will be produced by it. Moreover, the overcast will be produced, if the waterdrop of wavelength extent of light or the magnitude beyond it adheres to windshield insides, such as a windowpane inside of the building cooled by the open air, and an automobile, or the front face of glasses and light is scattered on it by the waterdrop. These are because minute waterdrop adheres to the glass front face which should be transparence essentially.

[0003] The front face of the glass used for a mirror or an aperture shows the middle property (it is about 50-90 degrees at the contact angle of pure water) of a hydrophilic property and hydrophobicity, and the fundamental cause of this problem originates in a drop adhering to a glass front face in the shape of a semi-sphere. A metal with the wettability equivalent [such a problem] to glass not only to glass but water, the ceramics, or plastics of a certain kind may happen similarly.

[0004] Thus, in order to solve the problem which blooms cloudy by adhesion of a drop with a minute front face, the film of a hydrophilic property was formed in the front face of glass or plastics, and the method of making fog resistance discover by making it not become semi-sphere-like, even if waterdrop adheres etc. has been proposed. Specifically, the approach of carrying out hydrophilization processing of the front face of glass or plastics with organic cationic surface active agents, such as A dimethyl alkylammonium chloride, the method of sticking on the front face of glass or plastics the transparence resin film which scoured B surface active agent and titanium oxide, etc. have been proposed.

[0005] Moreover, porous inorganic film (an alumina, alumina-silica system, etc.) was formed in front faces, such as C glass and plastics, and the method of aiming at improvement in a hydrophilic property with surface irregularity etc. has been tried.

[0006] However, in the approach of A, since the adhesion force of a surfactant was weak, when it used for a windowpane or the windshield of an automobile, there was a problem the hydrophilic effectiveness and whose antifog effectiveness a surfactant component ****s immediately and are lost. Moreover, by the approach of B, the surfactant component was eluted from the transparence resin film, the hydrophilic effectiveness decreased and there was a problem which a transparence resin film deteriorates in sunlight and loses transparency.

[0007] The approach of C) can expect improvement in endurance to some extent compared with the approach of using the above-mentioned organic film. However, by such film, in order to raise the antifog effectiveness, when membranous porosity was made to increase, the problem to which the reinforcement of the film itself and the adhesion reinforcement of the film and a substrate become low and which carries out property top phase conflict arose in many cases.

[0008] Moreover, although the approach of heating, drying or sintering is usually used after adjusting the ceramic

slurry containing impalpable powder, such as a silica and an alumina, and applying a slurry to the front face of glass or plastics with a dip method, a doctor blade method, etc. when forming the porosity inorganic film, it is difficult to arrange the pore diameter of the pore contained in the film by the film made by this approach, and it is usually that the hole which is dozens of micrometers surely exists. Thus, when the big hole existed in the film front face, there was a problem to which it becomes difficult for particles which float in air, such as tar of tobacco and various dust, to be fitted in and crowded in this hole, and to remove these in easy washing.

[0009]

[Problem(s) to be Solved by the Invention] This invention cancels the above-mentioned fault which the conventional technique has, and membranous reinforcement is high and it aims at offer of the anti-fogging film which is excellent also in adhesion with a base, and a base with an anti-fogging film. This invention aims at offer of said anti-fogging film to which dirt tends to fall, and a base with an anti-fogging film again.

[0010]

[Means for Solving the Problem] The inside of the bipolar membrane which this invention becomes from the pillar-shaped phase of a large number which grew in single dimension on the base, and the matrix phase which encloses it, It is the anti-fogging film which has the pore of a large number which were surrounded with the wall which continues from one membranous front face to the front face of another side, and which are penetrated in single dimension formed by removing the pillar-shaped phase which grew in single dimension, and the anti-fogging film characterized by the contact angle over water being 30 degrees or less is offered.

[0011] In this invention, a matrix phase serves as an ingredient which constitutes an anti-fogging film, and this matrix phase is a substantia-compacta object. The anti-fogging film of this invention is formed in two steps of processes. That is, the pillar-shaped phase which formed the bipolar membrane which consists of a pillar-shaped phase of a large number which grew in single dimension, and a matrix phase which encloses it, next grew like a single dimension in the bipolar membrane on the second stage story is removed by etching, and only a matrix phase is made to remain on a first stage story.

[0012] As an approach of forming bipolar membrane in a first stage story How to form directly the bipolar membrane which consists of a pillar-shaped phase which grew in single dimension, and a matrix phase which encloses it by the physical forming-membranes method (henceforth the first formation approach of bipolar membrane), The amorphous precursor film is first formed on a base, and then the approach (henceforth the second formation approach of bipolar membrane) of forming the bipolar membrane which consists an eutectic reaction of a lifting, and the pillar-shaped phase which grew in single dimension by this and the matrix phase which encloses it is listed by heat treatment.

[0013] Drawing 1 is the mimetic diagram showing the procedure which forms the anti-fogging film of this invention. a-d shows among drawing the procedure which forms the anti-fogging film of this invention using the first formation approach of bipolar membrane. The condition in which a formed the bipolar membrane 4 which consists of a pillar-shaped phase 2 and a matrix phase 3 by the physical forming-membranes method on the base 1 (first stage), The condition (middle) in which b formed bipolar membrane 4 similarly, the condition in which formation of bipolar membrane 4 ended c, and d remove the pillar-shaped phase 2 which grew in single dimension by selective etching, and the condition that the anti-fogging film 5 of this invention was formed is shown, respectively.

[0014] Moreover, e-h shows the procedure which forms the anti-fogging film of this invention using the second formation approach of bipolar membrane. The condition in which the amorphous precursor film 6 with which e contains transition metals was formed on the base 1, An eutectic reaction interface moves the condition that, as for f, eutectic structure was formed in the film front face of heat treatment, and g, to the film and a substrate interface by oxygen diffusion from a front face. The eutectic structure which consists of a pillar-shaped phase (transition-metals oxide crystal) 2 which finally grew in single dimension, and a matrix phase 3 which encloses it is formed. The condition which was able to do bipolar membrane 4, and h remove the pillar-shaped phase 2 which grew in single dimension by selective etching, and the condition that the anti-fogging film 5 of this invention was formed is shown, respectively.

[0015] In the first formation approach of bipolar membrane, a spatter, vacuum deposition, a CVD method, the laser ablation method, a molecular beam epitaxy method, etc. are mentioned as a physical forming-membranes method which forms bipolar membrane. Also in this, in addition to that it is easy to obtain the precise film and the film with high adhesion with a base being obtained, the spatter is excellent in mass-production nature or large area membrane formation nature, and especially desirable.

[0016] Although it is not limited especially as an approach of constituting a target using the ingredient which forms a pillar-shaped phase, and the ingredient which forms a matrix phase when forming bipolar membrane by the sputter, what mixed the powder of the ingredient which forms a pillar-shaped phase, and the powder of the ingredient which forms a matrix phase can be used as a target.

[0017] Moreover, many wafers with a magnitude of about several mm which consists of an ingredient which forms a matrix phase on the target which consists of an ingredient which forms a pillar-shaped phase are arranged, and what was used as the multicomponent target can be used suitably. Many wafers with a magnitude of about several mm which consists of an ingredient which forms a pillar-shaped phase on the target which consists of an ingredient which forms a matrix phase on the contrary are arranged, and what was used as the multicomponent target can be used suitably.

[0018] When producing bipolar membrane by the first formation approach of bipolar membrane, as a combination of the ingredient of a pillar-shaped phase and a matrix phase, the ingredient of a pillar-shaped phase and the ingredient of a matrix phase should just be the combination which starts phase separation at the time of film production. In this invention, the metal or alloy which is the metal which is easy to grow in the shape of a column as an ingredient of a pillar-shaped phase, and dissolves in an acid, alkali, etc. easily and which binding energy with the ingredient of a matrix phase is easy to be returned to it small in order to use the matrix phase which encloses a pillar-shaped phase for the pore part after etching a pillar-shaped phase as a residual phase is desirable.

[0019] One or more sorts chosen from the alloy which makes a principal component alkaline earth metal, such as an alloy and Mg, and it which make a principal component 3d transition metals, such as V, Cr, Mn, nickel, Fe, Co, Cu, and Zn, and it in consideration of the ease of the handling at the time of a sputter practical as an example of the ingredient of a pillar-shaped phase are mentioned. In addition, aluminum, In, Sn, Pb, etc. can be used.

[0020] as the example of the matrix phase used as a residual phase -- metals, such as nitrides, such as borides, such as carbide, such as oxide, such as a silica, an alumina, a titania, a mullite, cordierite, a spinel, a zeolite, and forsterite, silicon carbide, titanium carbide, and zirconium carbide, titanium boride, zirconium boride, and boron carbide, silicon nitride, titanium nitride, and zirconium nitride, and Cr, nickel, Cu, Au, aluminum, Pt, -- since -- one or more sorts chosen are mentioned.

[0021] In the first formation approach of bipolar membrane, the detailed organization for which the matrix phase enclosed the surroundings of the pillar-shaped phase which grew in single dimension is formed by controlling the mixing ratio and membrane formation conditions of an ingredient of a pillar-shaped phase and a matrix phase. For example, when forming bipolar membrane by the sputter, the average diameter of the pillar-shaped phase which grows changes with the volume fraction and membrane formation conditions (Ar gas pressure at the time of a sputter) of a pillar-shaped phase and a matrix phase.

[0022] Since the diameter of single dimension penetration pore is mostly in agreement with the diameter of the pillar-shaped phase which grows in single dimension, the average aperture of the single dimension penetration pore of the anti-fogging film of this invention finally obtained after etching is changeable with the mixing ratio and membrane formation conditions of an ingredient of a pillar-shaped phase and a matrix phase (Ar gas pressure, substrate temperature, etc. at the time of a sputter). For example, in the case of Co-SiO₂ system, to the particle size of Co in the film which produced the film with 2Pa Ar gas pressure being 8nm, when a film is produced with 8Pa Ar gas pressure, it is checked that the particle size of Co is set to about 40nm.

[0023] In the second formation approach of bipolar membrane, plating etc. can be used for solution methods, such as the physical forming-membranes methods, such as a sputter, vacuum deposition, a CVD method, the laser ablation method, and a molecular beam epitaxy method, and a sol-gel method, the spray pyrolysis method or the applying method, and a pan as an approach of forming the amorphous precursor film. Also in this, in addition to that it is easy to obtain the precise film and the film with high adhesion with a base being obtained, the sputter is excellent in mass-production nature or large area membrane formation nature, and especially desirable.

[0024] Although it is not limited especially as an approach of constituting a target using the ingredient which forms a pillar-shaped phase, and the ingredient which forms a matrix phase when forming the amorphous precursor film by a sputter etc., what mixed the powder of the ingredient which forms a pillar-shaped phase, and the powder of the ingredient which forms a matrix phase can be used as a target. For example, when forming the amorphous precursor film of a Fe-Si-O system, what mixed FeO powder and SiO₂ powder can be used as a target.

[0025] In the second formation approach of bipolar membrane, there are the as other metallic element and the oxygen as a combination of an element which are contained in the amorphous precursor film formed first as transition metals.

Be [what is necessary / just although it dissociates with other metals contained in the film and becomes a separate compound phase after heat treatment as an example of transition metals] rare earth elements, such as an alloy which uses 3d transition metals, such as V, Cr, Mn, nickel, Fe, Co, Cu, and Zn, and these metals as a principal component in consideration of the ease of the handling at the time of heat treatment etc., and the other multiple-valued cations Ce, Nd, Sm, and Er, -- since -- one or more sorts chosen are mentioned.

[0026] What is necessary is just not to react with transition metals at the time of heat treatment continuously performed as metallic elements other than transition metals. Since this metallic element serves as a component which constitutes the film which serves as a matrix phase which encloses a pillar-shaped phase (transition-metals compound needle crystal) at the time of heat treatment, and has single dimension penetration pore after etching, it is chosen by the membranous use purpose. For example, Si, aluminum, Mg, Zr, Sn, In, etc. are mentioned.

[0027] When carrying out spatter membrane formation of the amorphous precursor film, the diameter of the pillar-shaped phase which grows in single dimension by heat-treatment performed behind changes with the Ar gas pressure at the time of a spatter. For example, if the film which produced the film with 2Pa Ar gas pressure is heat-treated at 600 degrees C in the case of the film of a Fe-Si-O system, hematite (Fe_2O_3) with a diameter of about 4nm deposits, but when a film is produced with 8Pa Ar gas pressure, if same processing is performed, hematite with a diameter of about 20nm deposits. Since the diameter of single dimension penetration pore is mostly in agreement with the diameter of the pillar-shaped phase which grows in single dimension, the average aperture of the single dimension penetration pore of the anti-fogging film of this invention finally obtained after etching is controllable by membrane formation conditions (Ar gas pressure at the time of a spatter).

[0028] The amorphous precursor film containing transition metals, the other metal, and oxygen is heat-treated, and the eutectic decomposition reaction in which a transition-metals oxide and the oxide of the other metal carry out a separation deposit is made to cause in the second formation approach of bipolar membrane. It is important for the two phase deposit from this amorphous phase to happen from a film front face to coincidence moreover. What is necessary is just the conditions from which an eutectic decomposition reaction occurs as processing conditions when heating. namely, the temperature from which an eutectic decomposition reaction occurs about temperature -- in addition -- and a reaction should just be the temperature which advances at sufficient rate. Specifically, the temperature of about 400-650 degrees C is desirable.

[0029] In order to trigger an eutectic decomposition reaction, it is necessary to change the valence of transition metals. Two, the case where the amorphous precursor film is processed in the ambient atmosphere of an oxidizing quality, and the method of processing in the ambient atmosphere of reducibility, are possible as this approach. In the case of the eutectic reaction of an oxide, if it processes by reducing atmosphere, ununiformity nucleation is carried out and uniform eutectic structure may not be formed. In this case, uniform eutectic structure can be formed by heat-treating under an oxidizing atmosphere.

[0030] On a second stage story, using an acid or alkali, only the pillar-shaped phase extended in single dimension is etched alternatively, and is removed from the bipolar membrane formed on the first stage story. The thing suitable for removing alternatively only pillar-shaped phases, such as a sulfuric acid, a hydrochloric acid, a nitric acid, oxalic acid, and an acetic acid, as an acid used by this etching processing is chosen. For example, only metal cobalt is completely removable from the metal cobalt silica bipolar membrane produced by the first formation approach of bipolar membrane only by processing for several minutes in the nitric-acid water solution of 0.1 mols / L removing metal cobalt.

[0031] Moreover, in the case of the bipolar membrane of the Fe-Si-O system formed by the second formation approach of bipolar membrane, the hematite extended in single dimension can carry out selective etching by immersing the film in the water solution of a hydrochloric acid to being meltable, at the hydrochloric-acid water solution of about 6 mol/L, since the silica is insoluble in this solution.

[0032] It is the anti-fogging film which has the pore of a large number which were surrounded with the wall which the anti-fogging film of this invention is formed as mentioned above, and continues from one membranous front face to the front face of another side, and which are penetrated in single dimension, and the contact angle over water is the film 30 degrees or less. Antifog effectiveness with the contact angle sufficient by 30-degree ** over water is not acquired.

[0033] Although the anti-fogging film of this invention consists of one or more sorts chosen from an oxide, carbide, the boride, the nitride, and the metal and it is chosen according to an application, the viewpoint of endurance, reinforcement, chemical stability, the ease of forming, etc. to an oxide is the most desirable. Moreover, from a fog

resistance viewpoint, a silica is desirable.

[0034] Moreover, as for the average aperture of the pore penetrated in single dimension in the anti-fogging film of this invention, it is desirable that it is 1-500nm. In less than 1nm, sufficient antifog effectiveness is not acquired, antifog effectiveness sufficient in 500nm ** is not acquired, and also membranous reinforcement or adhesion with a base may also fall.

[0035] Furthermore, as for the specific surface area of the anti-fogging film of this invention, it is desirable that it is 20-2000m²/g. Under by 20m²/g, sufficient antifog effectiveness may not be acquired and sufficient film reinforcement may not be obtained at 2000m²/g **.

[0036] This invention offers the base with an anti-fogging film which has said anti-fogging film on a base again. When a substrate or films, such as glass, ceramics, a metal, and plastics, can be used as a base which forms the anti-fogging film of this invention when using the first formation approach of bipolar membrane, and using the second formation approach of bipolar membrane, a substrate or films, such as glass, ceramics, and a heat-resistant metal, can be used.

[0037] Oxidation-resistant alloys, such as stainless steel which consists of Fe, nickel, Cr, V, etc. as a heat-resistant metal, and Hastelloy, are suitable. Moreover, what is necessary is just to form the bipolar membrane by the first formation approach, or the amorphous precursor film by the second formation approach directly, if surface irregularity is not so intense when forming the anti-fogging film of this invention on the base which has irregularity on front faces, such as a porosity ceramic substrate. If a front face is ground, it is made smooth and the anti-fogging film of this invention is formed on a smooth base front face after filling up the irregularity on the front face of a base with the ingredient of resin and others when [that the irregularity on the front face of a base is intense] direct formation of the film of a first stage story is difficult, sufficient adhesion reinforcement is securable. The anti-fogging film of this invention can consist of various presentations. The anti-fogging film of this invention is suitable for the anti-fogging film used for the windshield of a car, the windowpane of a building, a mirror, an optical lens, etc.

[0038]

[Function] Since the pore which continues from a film front face exists to the interior of the film, the anti-fogging film of this invention has a high hydrophilic property in extent which the waterdrop adhering to a front face permeates to the interior of the film, and shows the antifog effectiveness practically.

[0039] Furthermore, since the continuous matrix phase encloses the surroundings of the penetration pore of a single dimension, the anti-fogging film of this invention has theoretically large film reinforcement compared with the former to a certain porosity inorganic film, and its adhesion with a base is also good. By the film of this invention, the matrix which encloses single dimension penetration pore depends that film reinforcement is large on it being really which continued completely a moldings to the conventional porosity inorganic anti-fogging film combining a ceramic particle loosely by sintering etc.

[0040] Moreover, also about adhesion with a substrate, if the bipolar membrane (including the amorphous precursor film by the second formation approach) of a first stage story is formed by a spatter etc., the high film of especially adhesion will be obtained. Moreover, although the problem to which the reinforcement of the film itself and the adhesion reinforcement of the film and a substrate become low and which carries out property top phase conflict arose in many cases when membranous porosity was made to increase in order that the conventional porosity inorganic film might raise the antifog effectiveness In the anti-fogging film of this invention, maintaining the high antifog effectiveness, both can make membranous reinforcement and adhesion with a base high, and the anti-fogging film which has fog resistance and high endurance can be realized.

[0041]

[Example] (Example 1) The bipolar membrane which consists of two phases of metals Co and SiO₂ was formed on the soda lime glass substrate with a thickness of 1.2mm using the first formation approach of bipolar membrane. On the occasion of the spatter, the multicomponent target which placed SiO₂ tip of 5mm angle on the metal Co target with a diameter of 15.24cm was used. The amount of SiO₂ chip was adjusted so that 20% of the total surface area of one side of a target might be occupied. After exhausting a vacuum tub up to 5x10⁻⁴ Pa, Ar gas is introduced, flow regulation was carried out and the plasma was generated by the RF input of 600W so that the gas pressure inside a vacuum tub might be set to 2Pa. Membrane formation rates are about 0.25 nm/sec, and neither positive substrate heating nor substrate bias impression was performed at the time of membrane formation. In addition, the substrate periphery gave the mask and did not form the film.

[0042] Thus, as a result of observing Co-SiO₂ formed bipolar membrane by TEM (transmission electron microscope),

Co crystal grain child with a mean particle diameter of about 10nm was growing in the shape of a column, and it was checked that the amorphous SiO₂ matrix phase encloses the surroundings of it.

[0043] Co-SiO₂ bipolar membrane of 500nm of thickness formed by the above-mentioned approach as a second stage story was etched into the nitric-acid water solution of 0.1 mol/L by being immersed for 5 minutes. As a result of observing the film after removing the pillar-shaped phase of Co by etching from Co-SiO₂ bipolar membrane by SEM (scanning electron microscope), Co pillar-shaped phase was eluted and it was checked that the SiO₂ matrix phase remains.

[0044] Drawing 2 is an isothermal adsorption-and-desorption curve in the liquid nitrogen temperature of the anti-fogging film formed as mentioned above. It has much pores whose anti-fogging films with which adsorption and desorption of clear nitrogen gas were seen and obtained from drawing in the differential pressure (P/P₀) = 0.6 neighborhood are the diameters of about 10nm, and it turns out that the specific surface area of the wall of a hole is about 1000m²/g (extent equivalent to activated carbon).

[0045] Moreover, when the waterdrop of pure water with a diameter of about 1mm was dropped at the front face of the obtained anti-fogging film and the contact angle was measured, it was about 15 degrees. Moreover, after having put the obtained anti-fogging film into the refrigerator the whole substrate, holding for 1 hour and cooling at about 5 degrees C, when it took out and exhalation was blown, minute waterdrop adhered to the glass front face which does not have the film in a part with the film to the overcast not arising, the overcast arose, and it became opaque.

[0046] When the Taber abrasion resistant test investigated the endurance of an above-mentioned anti-fogging film, change was not looked at by the contact angle of water, fog resistance ability, transparency, etc. even if it rotated 1000 times. In addition, the Taber abrasion resistant test is commercial CS10 mold Taber wearing-of-die ring and JIS. It carried out by applying a 500g load, rotating 1000 times by 60rpm using the abrasive paper of quality equivalent to the abrasive paper of AA of No. 180 specified to R6252, and wearing the film. The same is said of the Taber abrasion resistant test in the following examples.

[0047] (Example 1 of a comparison) After applying to a soda lime glass substrate front face the coating liquid which added and carried out viscosity control of the hydrochloric acid to the ethyl silicate water solution which distributed the polystyrene particle (mean particle diameter of 0.06 micrometers), it heated at about 400 degrees C, and the porosity silica film of 500nm of thickness was formed. When the same Taber abrasion resistant test as an example 1 investigated endurance, in 1000 times, a part of film exfoliated and transparency was spoiled.

[0048] (Example 2) Co-SiO₂ bipolar membrane of 500nm of thickness was formed like the example 1 except having made the membrane formation rate into about 0.3 nm/sec. Like Co-SiO₂ bipolar membrane obtained in the example 1, the structure inside this Co-SiO₂ bipolar membrane found that the mean particle diameter of Co crystal was large with about 20nm in this case, although the amorphous SiO₂ matrix phase enclosed the surroundings of Co crystal grain child's pillar-shaped phase.

[0049] The sample of 500nm of thickness produced by the above-mentioned approach was immersed in the nitric-acid water solution of 0.1 mol/L for 5 minutes, and dissolution removal of the Co pillar-shaped phase was carried out. Co pillar-shaped phase was eluted like the example 1, and the SiO₂ matrix phase remained. The contact angles over a membranous specific surface area and pure water are about 1000m²/g and 13 degrees, respectively, and it was checked that there is the antifog effectiveness almost equivalent to an example 1 by the experiment which blows exhalation.

[0050] (Example 3) Co-SiO₂ bipolar membrane was formed on the soda lime glass substrate with a thickness of 1.2mm as follows using the same multicomponent target as an example 1. That is, after exhausting a vacuum tub up to 5x10 to 4 Pa, Ar gas is introduced, flow regulation was carried out and the plasma was generated by the RF input of 800W so that the gas pressure inside a vacuum tub might be set to 8Pa. Membrane formation rates are about 0.6 nm/sec, and heated substrate temperature at 200 degrees C at the time of membrane formation.

[0051] Like Co-SiO₂ bipolar membrane obtained in the example 1, the structure inside this Co-SiO₂ bipolar membrane found that the mean particle diameter of Co crystal was large with about 100nm in this case, although the amorphous SiO₂ matrix phase enclosed the surroundings of Co crystal grain child's pillar-shaped phase.

[0052] The sample of 1500nm of thickness produced by the above-mentioned approach was immersed in the nitric-acid water solution of 0.1 mol/L for 15 minutes, and dissolution removal of the Co particle was carried out. Co pillar-shaped phase was eluted as well as the example 1, and the SiO₂ matrix phase remained. The contact angles over a membranous specific surface area and pure water are about 1000m²/g and 12 degrees, respectively, and it was checked that there is the antifog effectiveness almost equivalent to an example 1 by the experiment which blows exhalation.

[0053] (Example 4) Co-SiO₂ bipolar membrane was formed on the Hastelloy plate with a thickness of 2mm as follows using the same multicomponent target as an example 1. That is, after exhausting a vacuum tub up to 5x10 to 4 Pa, Ar gas is introduced, flow regulation was carried out and the plasma was generated by the RF input of 400W so that the gas pressure inside a vacuum tub might be set to 2Pa. Membrane formation rates are about 0.35 nm/sec, and neither intentional substrate temperature nor bias impression was performed at the time of membrane formation.

[0054] Although the amorphous SiO₂ matrix phase enclosed the surroundings of Co crystal grain child's pillar-shaped phase like Co-SiO₂ bipolar membrane obtained in the example 1 as for the structure inside this Co-SiO₂ bipolar membrane, the mean particle diameter of Co crystal was about 10nm in this case. The sample of 800nm of thickness produced by this approach was immersed in the nitric-acid water solution of 0.1 mol/L for 10 minutes, and dissolution removal of the Co particle was carried out. Co pillar-shaped phase was eluted as well as the example 1, and the SiO₂ matrix phase remained. The contact angles over a membranous specific surface area and pure water are about 1000m²/g and 12 degrees, respectively, and it was checked that there is the antifog effectiveness almost equivalent to an example 1 by the experiment which blows exhalation.

[0055] (Example 5) Co-SiO₂ bipolar membrane was formed on the alumina-ceramics substrate with a thickness of 5mm as follows using the same multicomponent target as an example 1. That is, after exhausting a vacuum tub up to 5x10 to 4 Pa, Ar gas is introduced, flow regulation was carried out and the plasma was generated by the RF input of 400W so that the gas pressure inside a vacuum tub might be set to 2Pa. Membrane formation rates are about 0.3 nm/sec, and neither intentional substrate temperature nor bias impression was performed at the time of membrane formation.

[0056] Although the amorphous SiO₂ matrix phase enclosed the surroundings of Co crystal grain child's pillar-shaped phase like Co-SiO₂ bipolar membrane obtained in the example 1 as for the structure inside this Co-SiO₂ bipolar membrane, the mean particle diameter of Co crystal was about 9nm in this case. The sample of 700nm of thickness produced by this approach was immersed in the nitric-acid water solution of 0.1 mol/L for 10 minutes, and dissolution removal of the Co particle was carried out. Co pillar-shaped phase was eluted as well as the example 1, and the SiO₂ matrix phase remained. The contact angles over a membranous specific surface area and pure water are about 1000m²/g and 16 degrees, respectively, and it was checked that there is the antifog effectiveness almost equivalent to an example 1 by the experiment which blows exhalation.

[0057] (Example 6) Co-SiO₂ bipolar membrane was formed on the polyethylene film sheet with a thickness of 1.8mm as follows using the same multicomponent target as an example 1. That is, after exhausting a vacuum tub up to 5x10 to 4 Pa, Ar gas is introduced, flow regulation was carried out and the plasma was generated by the RF input of 400W so that the gas pressure inside a vacuum tub might be set to 2Pa. Membrane formation rates are about 0.2 nm/sec, and neither intentional substrate temperature nor bias impression was performed at the time of membrane formation.

[0058] Although the amorphous SiO₂ matrix phase enclosed the surroundings of Co crystal grain child's pillar-shaped phase like Co-SiO₂ bipolar membrane obtained in the example 1 as for the structure inside this Co-SiO₂ bipolar membrane, the mean particle diameter of Co crystal was about 15nm in this case. The sample of 200nm of thickness produced by this approach was immersed in the nitric-acid water solution of 0.1 mol/L for 5 minutes, and dissolution removal of the Co particle was carried out. Co pillar-shaped phase was eluted as well as the example 1, and the SiO₂ matrix phase remained. The contact angles over a membranous specific surface area and pure water are about 1000m²/g and 28 degrees, respectively, and it was checked that there is the antifog effectiveness almost equivalent to an example 1 by the experiment which blows exhalation.

[0059] (Example 7) After applying the epoxy resin on the porosity silica plate with a thickness of 2mm and stiffening it, the substrate front face was ground with diamond polish equipment, and the smooth polished surface was acquired. On this substrate, Co-SiO₂ bipolar membrane was formed as follows using the same multicomponent target as an example 1. That is, after exhausting a vacuum tub up to 5x10 to 4 Pa, Ar gas is introduced, flow regulation was carried out and the plasma was generated by the RF input of 400W so that the gas pressure inside a vacuum tub might be set to 2Pa. Membrane formation rates are about 0.35 nm/sec, and neither positive substrate heating nor substrate bias impression was performed at the time of membrane formation.

[0060] Although the amorphous SiO₂ matrix phase enclosed the surroundings of Co crystal grain child's pillar-shaped phase like Co-SiO₂ bipolar membrane obtained in the example 1 as for the structure inside this Co-SiO₂ bipolar membrane, the mean particle diameter of Co crystal was about 9nm in this case. The sample of 300nm of thickness produced by this approach was immersed in the nitric-acid water solution of 0.1 mol/L for 5 minutes, and dissolution

removal of the Co particle was carried out. Co pillar-shaped phase was eluted as well as the example 1, and the SiO₂ matrix phase remained. The contact angles over a membranous specific surface area and pure water are about 1000m²/g and 8 degrees, respectively, and it was checked that there is the antifog effectiveness almost equivalent to an example 1 by the experiment which blows exhalation.

[0061] (Example 8) On soda lime glass with a thickness of 1.2mm, Co-TiO₂ bipolar membrane was formed as follows. On the occasion of the spatter, the multicomponent target which placed TiO₂ tip of 0.5mm angle on the metal Co target with a diameter of 15.24cm was used. The amount of TiO₂ chip was adjusted so that 30% of the total surface area of one side of a target might be occupied. After exhausting a vacuum tub up to 5x10 to 4 Pa, Ar gas is introduced, flow regulation was carried out and the plasma was generated by the RF input of 400W so that the gas pressure inside a vacuum tub might be set to 2Pa. Membrane formation rates are about 0.4 nm/sec, and neither positive substrate heating nor substrate bias impression was performed at the time of membrane formation.

[0062] Although the amorphous TiO₂ matrix phase enclosed the surroundings of Co crystal grain child's pillar-shaped phase like Co-SiO₂ bipolar membrane obtained in the example 1 as for the structure inside this Co-TiO₂ bipolar membrane, the mean particle diameter of Co crystal was about 8nm in this case. The sample of 250nm of thickness produced by this approach was immersed in the nitric-acid water solution of 0.1 mol/L for 5 minutes, and dissolution removal of the Co particle was carried out. Co pillar-shaped phase was eluted as well as the example 1, and the TiO₂ matrix phase remained. The contact angles over a membranous specific surface area and pure water are about 1000m²/g and 28 degrees, respectively, and it was checked that there is the antifog effectiveness almost equivalent to an example 1 by the experiment which blows exhalation.

[0063] moreover, the place which heated among air TiO₂ amorphous film obtained after etching at 600 degrees C for 1 hour -- the anatase of a crystalline substance -- changing -- in addition -- and a membranous specific surface area was hardly changing.

[0064] (Example 9) On soda lime glass with a thickness of 1.2mm, Co-SiC bipolar membrane was formed as follows. On the occasion of the spatter, the multicomponent target which placed the SiC tip of 0.5mm angle on the metal Co target with a diameter of 15.24cm was used. The amount of a SiC chip was adjusted so that 40% of the total surface area of one side of a target might be occupied. After exhausting a vacuum tub up to 5x10 to 4 Pa, Ar gas is introduced, flow regulation was carried out and the plasma was generated by the RF input of 800W so that the gas pressure inside a vacuum tub might be set to 2Pa. Membrane formation rates are about 0.3 nm/sec, and neither positive substrate heating nor substrate bias impression was performed at the time of membrane formation.

[0065] Although the amorphous SiC matrix phase enclosed the surroundings of Co crystal grain child's pillar-shaped phase like Co-SiO₂ bipolar membrane obtained in the example 1 as for the structure inside this Co-SiC bipolar membrane, the mean particle diameter of Co crystal was about 6nm in this case. The sample of 250nm of thickness produced by this approach was immersed in the nitric-acid water solution of 0.1 mol/L for 5 minutes, and dissolution removal of the Co particle was carried out. Co pillar-shaped phase was eluted as well as the example 1, and the SiC matrix phase remained. The contact angles over a membranous specific surface area and pure water are about 1000m²/g and 28 degrees, respectively, and it was checked that there is the antifog effectiveness almost equivalent to an example 1 by the experiment which blows exhalation.

[0066] (Example 10) On soda lime glass with a thickness of 1.2mm, Co-Si₃N₄ bipolar membrane was formed as follows. On the occasion of the spatter, the multicomponent target which placed Si₃N₄ tip of 0.5mm angle on the metal Co target with a diameter of 15.24cm was used. The amount of Si₃N₄ chip was adjusted so that 40% of the total surface area of one side of a target might be occupied. After exhausting a vacuum tub up to 5x10 to 4 Pa, Ar gas is introduced, flow regulation was carried out and the plasma was generated by the RF input of 800W so that the gas pressure inside a vacuum tub might be set to 2Pa. Membrane formation rates are about 0.3 nm/sec, and neither positive substrate heating nor substrate bias impression was performed at the time of membrane formation.

[0067] Although the amorphous Si₃N₄ matrix phase enclosed the surroundings of Co crystal grain child's pillar-shaped phase like Co-SiO₂ bipolar membrane obtained in the example 1 as for the structure inside this Co-Si₃N₄ bipolar membrane, the mean particle diameter of Co crystal was about 6nm in this case. The sample of 250nm of thickness produced by this approach was immersed in the nitric-acid water solution of 0.1 mol/L for 5 minutes, and dissolution removal of the Co particle was carried out. Co pillar-shaped phase was eluted as well as the example 1, and the Si₃N₄ matrix phase remained. The contact angles over a membranous specific surface area and pure water are about 1000m²/g and 28 degrees, respectively, and it was checked that there is the antifog effectiveness almost equivalent to

an example 1 by the experiment which blows exhalation.

[0068] (Example 11) On soda lime glass with a thickness of 1.2mm, Co-Cr bipolar membrane was formed as follows. On the occasion of the spatter, the multicomponent target which placed Cr tip of 0.5mm angle on the metal Co target with a diameter of 15.24cm was used. The amount of Cr chip was adjusted so that 40% of the total surface area of one side of a target might be occupied. After exhausting a vacuum tub up to 5×10^{-4} Pa, Ar gas is introduced, flow regulation was carried out and the plasma was generated by the RF input of 800W so that the gas pressure inside a vacuum tub might be set to 2Pa. Membrane formation rates are about 0.3 nm/sec, and neither positive substrate heating nor substrate bias impression was performed at the time of membrane formation.

[0069] although, as for the structure inside this Co-Cr bipolar membrane, the matrix phase which consists of the Cr crystal aggregate encloses the surroundings of Co columnar crystal particle (pillar-shaped phase) like Co-SiO₂ bipolar membrane obtained in the example 1 -- in this case -- the mean particle diameter of Co crystal -- about 6nm it was. The sample of 250nm of thickness produced by this approach was immersed in the nitric-acid water solution of 0.1 mol/L for 5 minutes, and dissolution removal of the Co particle was carried out. Co pillar-shaped phase was eluted as well as the example 1, and Cr matrix phase remained. The contact angles over a membranous specific surface area and pure water are about 1000m²/g and 28 degrees, respectively, and it was checked that there is the antifog effectiveness almost equivalent to an example 1 by the experiment which blows exhalation.

[0070] (Example 12) On soda lime glass with a thickness of 1.2mm, Co-ZrB₂ bipolar membrane was formed as follows. On the occasion of the spatter, the multicomponent target which placed the ZrB₂ ceramic tip of 1cm angle on the metal Co target with a diameter of 15.24cm was used. The amount of a ZrB₂ ceramic chip was adjusted so that 40% of the total surface area of one side of a target might be occupied. After exhausting a vacuum tub up to 5×10^{-4} Pa, Ar gas is introduced, flow regulation was carried out and the plasma was generated by the RF input of 600W so that the gas pressure inside a vacuum tub might be set to 2Pa. Membrane formation rates are about 0.38 nm/sec, and neither positive substrate heating nor substrate bias impression was performed at the time of membrane formation.

[0071] Although the amorphous ZrB₂ matrix phase enclosed the surroundings of Co crystal grain child's pillar-shaped phase like Co-SiO₂ bipolar membrane obtained in the example 1 as for the structure inside this Co-ZrB₂ bipolar membrane, the mean particle diameter of Co crystal was about 10nm in this case. The sample of 450nm of thickness produced by this approach was immersed in the nitric-acid water solution of 0.1 mol/L for 5 minutes, and dissolution removal of the Co particle was carried out. Co pillar-shaped phase was eluted as well as the example 1, and the ZrB₂ matrix phase remained. The contact angles over a membranous specific surface area and pure water are about 1000m²/g and 22 degrees, respectively, and it was checked that there is the antifog effectiveness almost equivalent to an example 1 by the experiment which blows exhalation.

[0072] (Example 13) The amorphous precursor film which consists of three components of Fe-Si-O was formed by the spatter on the heat-resisting glass (Corning #7059) substrate with a thickness of 1.0mm. What mixed and sintered 3OF₄ powder and SiO₂ powder at 70% and 30% of a rate by the volume ratio in the spatter, respectively was used for the target. After exhausting a vacuum tub up to 5×10^{-4} Pa, argon gas was introduced, the flow rate of Ar gas was adjusted so that the gas pressure inside a vacuum tub might be set to 2Pa, the RF of 4.4 W/cm² was inputted, and the plasma was generated. The membrane formation rates at this time were about 0.2 nm/sec.

[0073] When the amorphous precursor film which formed membranes was observed by SEM, the amorphous film with a thickness of about 120nm was formed on the glass substrate. Defects, such as a crack and pore, were not seen in the amorphous film, but the very precise film was formed. Then, this amorphous film was heat-treated at 600 degrees C among air for 2 hours. When Fe₂O₃-SiO₂ bipolar membrane formed of heat-treatment was observed by TEM, it was checked that the needlelike hematite (Fe₂O₃) crystal extended in single dimension and the silica (SiO₂) which encloses the surroundings of it form eutectic structure. The hematite crystal was extended at right angles to a film front face toward the interface with a substrate from the film front face, and the diameter was about 4nm.

[0074] Finally, it was immersed in the hydrochloric-acid water solution of about 6 mol/L at the room temperature the whole substrate for 48 hours, and only hematite removed the film heat-treated by the above-mentioned approach. When the cross section of the anti-fogging film which removed hematite and was able to do it was observed by TEM, an amorphous silica matrix and the penetration pore extended in single dimension were observed. The diameter of penetration pore is the almost same 4nm as the diameter of the hematite before acid treatment, and it was checked that this penetration pore exists in the silica film. The contact angles over a membranous specific surface area and pure water are about 800m²/g and 8 degrees, respectively, and it was checked that there is the antifog effectiveness almost

equivalent to an example 1 by the experiment which blows exhalation.

[0075] (Example 14) The amorphous precursor film which consists of three components of Fe-Si-O was formed by the sputter on the heat-resisting glass (Corning #7059) substrate with a thickness of 1.0mm. What mixed and sintered 3OFe_4 powder and SiO_2 powder at 70% and 30% of a rate by the volume ratio in the sputter, respectively was used for the target. After exhausting a vacuum tub up to 5×10^{-4} Pa, argon gas was introduced, the flow rate of Ar gas was adjusted so that the gas pressure inside a vacuum tub might be set to 8Pa, the RF of 4.4 W/cm² was inputted, and the plasma was generated. The membrane formation rates at this time were about 0.1 nm/sec.

[0076] When the amorphous precursor film which formed membranes was observed by SEM, the almost same amorphous film as an example 13 was formed by about 80nm in thickness on the glass substrate. Defects, such as a crack and pore, were not seen in the amorphous film, but the very precise film was formed. Then, this amorphous film was heat-treated at 600 degrees C among air for 2 hours. When Fe_2O_3 - SiO_2 bipolar membrane formed of heat-treatment was observed by TEM, the needlelike hematite extended in single dimension and the silica which encloses the surroundings of it formed eutectic structure like the example 13. The hematite crystal was extended at right angles to a film front face toward the interface with a substrate from the film front face, and the diameter was about 20nm.

[0077] Finally, it was immersed in the hydrochloric-acid water solution of about 6 mol/L at the room temperature the whole substrate for 48 hours, and only hematite removed the film heat-treated by the above-mentioned approach. When gazed at the detailed organization of a film cross section by TEM, it was checked that the penetration pore of the almost same diameter as the diameter of the hematite before acid treatment exists in the silica film. The contact angles over a membranous specific surface area and pure water are about 1200m²/g and 5 degrees, respectively, and it was checked that there is the antifog effectiveness almost equivalent to an example 1 by the experiment which blows exhalation.

[0078] (Example 2 of a comparison) The amorphous precursor film obtained in the example 13 was heat-treated at 800 degrees C among air for 1 hour. the result of having observed the film after heat-treatment by TEM -- a hematite crystal -- not needlelike -- the diameter of about 10nm -- it is spherical, and it deposited so that it might be wrapped in a silica matrix. Then, although the film heat-treated by the above-mentioned approach was immersed in the hydrochloric-acid water solution of about 6 mol/L the whole substrate, also 100 hours after, no hematite crystals were able to be removed.

[0079]

[Effect of the Invention] Holding high fog resistance ability, since the anti-fogging film of this invention has the pore of a large number which were surrounded with the wall which continues from one membranous front face to the front face of another side and which are penetrated in single dimension, its membranous reinforcement is high and it is excellent also in adhesion with a base. Moreover, the anti-fogging film of this invention can be applied to the base of varieties, and can consist of various presentations.

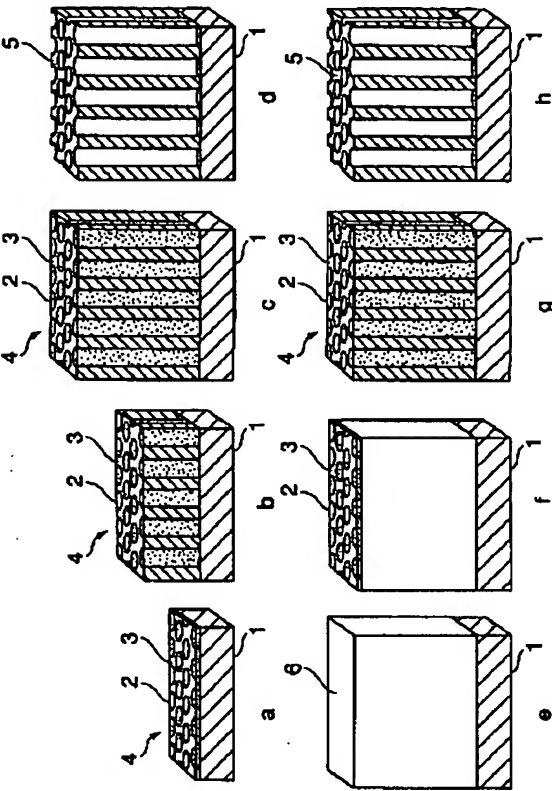
[0080] Moreover, the diameter of the pore contained in the anti-fogging film of this invention has gathered mostly in about 1-500nm, and an about dozens of micrometers huge hole does not exist. Therefore, particles which float in air, such as tar of tobacco and various dust, fit in, and are not crowded, and these can be removed by easy washing.

[0081] When the anti-fogging film of this invention uses an oxide, carbide, a boride, and a nitride as a principal component, it is suitable for anti-fogging films for cloudy prevention, such as a mirror, a structural windowpane, a windshield of an automobile, or an optical lens front face, etc. Moreover, when using metals, such as Cr, nickel, Cu, Au, aluminum, and Pt, as a principal component, it is suitable for a reflecting mirror, the surface coat of mirror on a curved road, the anti-fogging film for coatings for infrared reflection, etc.

[0082] Since the anti-fogging film of this invention has the pore penetrated from a front face to the interior of the film and has a big specific surface area, it can add an antifouling function by photodissociating the organic substance which added the catalyst function and the catalyst support function, and adhered to the front face etc., and can also use it as the film with which fog resistance continues indefinitely.

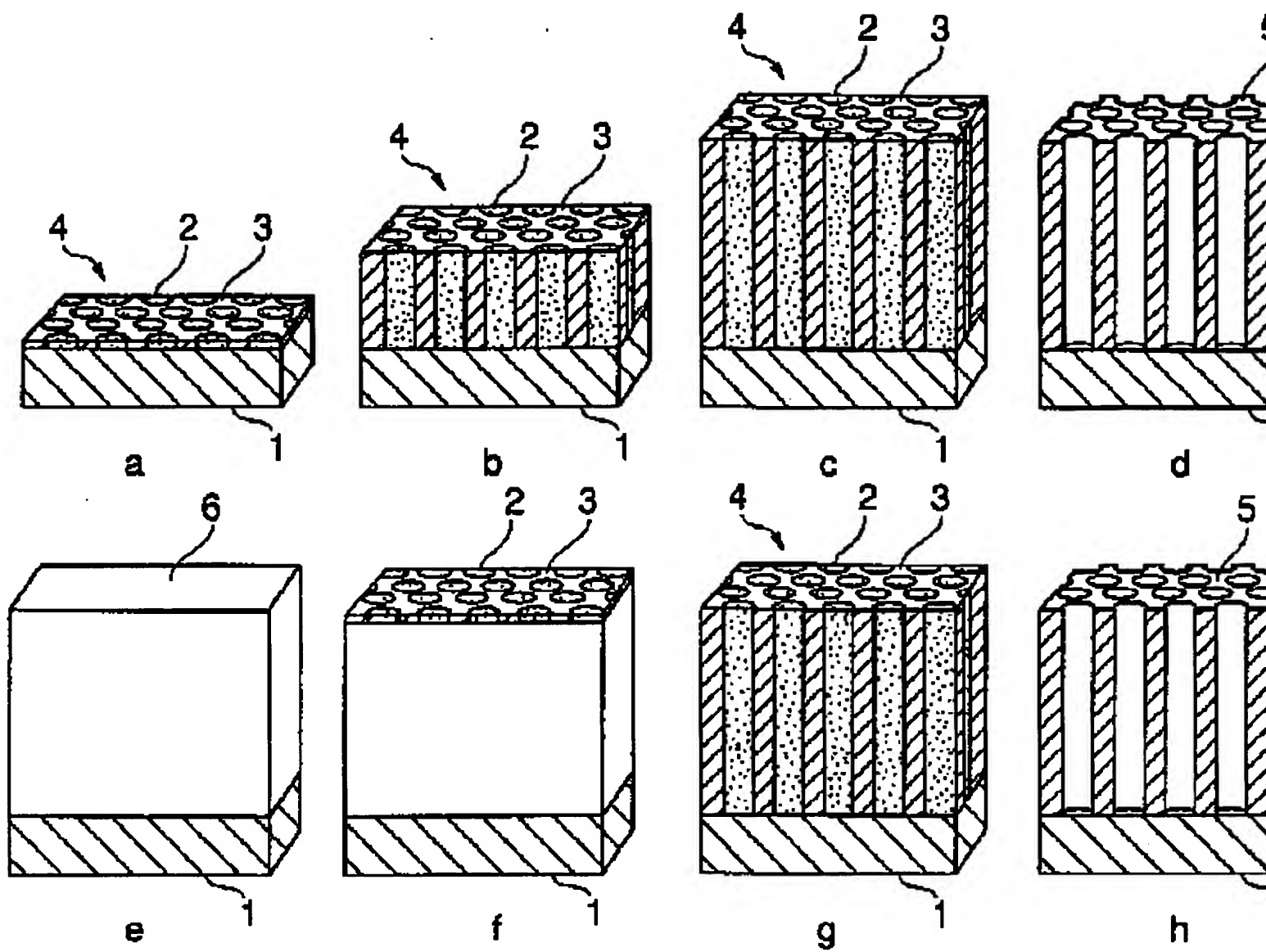
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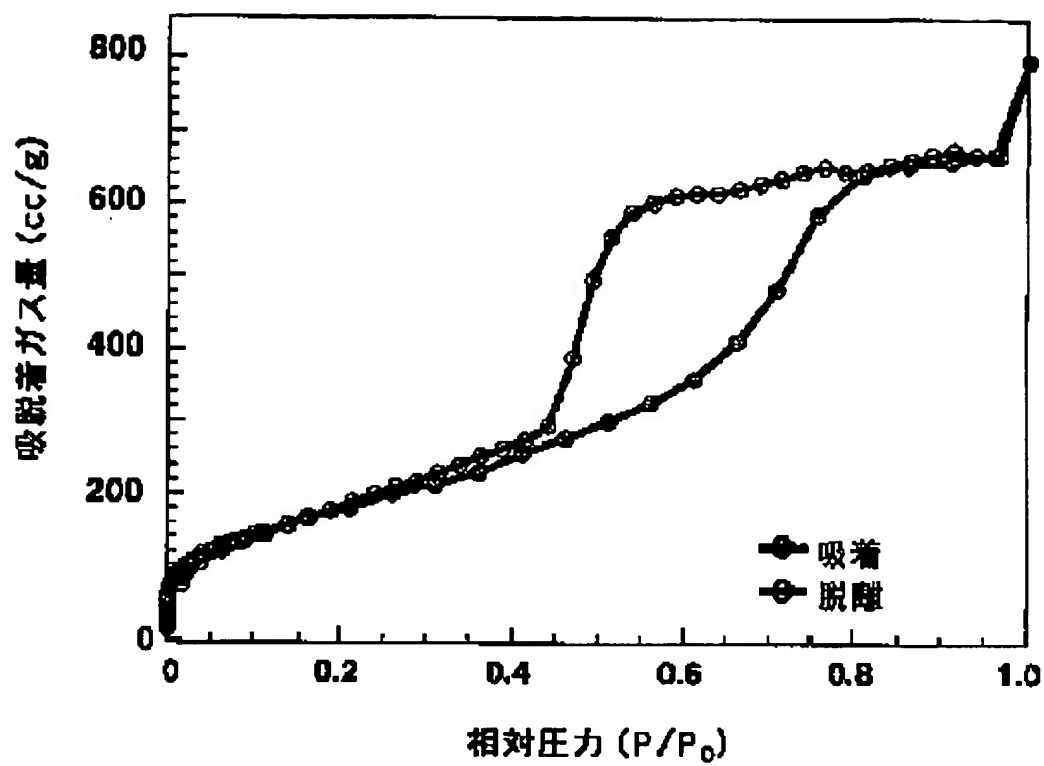


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